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"SYNTHESIS AND PROPERTIES OF A THERMOTROPIC COPOLYESTER BASED
ON 4,4'-DIHYDROXY-α,α'-DIMETHYLBENZALAZINE"

BY

A. L. CIMECIOGLU, H. FRUITWALA, AND R. A. WEISS

LIQUID CRYSTALLINE POLYMER RESEARCH CENTER
UNIVERSITY OF CONNECTICUT
STORRS, CT 06269-3136

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Dr. Kenneth J. Wynne	(202) 696-4410	ONR

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Synthesis and Properties of a Thermotropic copolyester based on 4,4'-dihydroxy-α,α'-dimethylbenzalazine

A. Levent Cimecioglu, Hitesh Fruitwala, R. A. Weiss*

Polymer Science Program and Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269-3136 USA

SUMMARY:

The synthesis of a thermotropic copolyester based on 4,4'-dihydroxy-α,α'-dimethylbenzalazine and 50/50 molar composition of sebacoyl/dodecanedioyl dichlorides was investigated in chloroform via a low temperature solution route. Polymers with η_{inh} between 0,27 - 1,56 dlg^{-1} were characterised by ^{1}H NMR, IR, thermal analyses, GPC and static light scattering techniques. Enantiotropic polymers exhibited a large mesophase range ($\sim$ 100°C) and the values of both crystal-nematic and nematic-isotropic transitions were molecular weight dependent. Intrinsic viscosity was determined to relate to molecular weight by $[\eta] = 9,6 \times 10^{-4} \cdot \overline{M}_w^{0,68}$ in chloroform at 25°C, and the persistence length was calculated to be of the order of 27A$^\circ$.

Introduction

Thermotropic mesomorphism exhibited by organic compounds has been known and studied extensively for over a century[1]. However, it was not until the mid-1970's that the thermotropic behaviour of polymeric liquid crystals (PLCs) was demonstrated[2]. Since then, there has been an ever increasing interest in this field, reflected by an explosion in publications and patents issued, as well as the commercialisation of several PLCs. Research on thermotropic PLCs can be divided into two broad categories: i) main chain PLCs and ii) side chain PLCs. The former field has also branched into several different areas largely as a result of the efforts to reduce the usually very high transition temperatures. One of these involves the incorporation of flexible spacers in the main chain, a subject that was recently reviewed by Ober et al.[3].

Roviello and Sirigu[2,4], first demonstrated thermotropic behaviour in polymers with semi-flexible polyester PLCs based on the mesogen 4,4'-dihydroxy-α,α'-dimethylbenzalazine. These nematic polyesters had relatively low transition temperatures and were soluble. Among other things, the authors also established that by using two different aliphatic spacers, the melting transition could be lowered significantly while the clearing temperatures remained more or less unchanged[5]. The biggest effect occured for a 50/50 mole ratio of the spacers.

Several research programs in our laboratory have used an LC copolymer, first synthesised by Roviello and Sirigu[6], based on this mesogenic core and a 50/50 molar composition of $-OOC-(CH_2)_8-COO-$ and $-OOC-(CH_2)_{10}-COO-$ flexible spacers. This polymer was previously used in studies of self-reinforcing polymer blends[7,8] and is currently being used in small angle neutron scattering studies of the molecular conformation of a PLC in the nematic state[9]. In this latter work, it is essential that the

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polymer is well characterised, especially in terms of its molecular weight and thermal properties. This paper describes the synthesis of polymers via a solution polycondensation route that was employed in order to control the polymer molecular weights and the evaluation of their basic properties.

Experimental part

Materials: Hydrazine monohdyrate (from Eastman Kodak Chemicals), 4-hydroxyacetophenone , pyridine, triethylamine and chloroform (HPLC) (from Aldrich) were used as supplied. N-methylpyrrolidone (NMP) (from Aldrich) was dried by refluxing over calcium hydride, distilled and stored over Type 3A molecular sieves. Sebacoyl chloride and dodecanedioyl dichloride (from Aldrich) were purified by vacuum distillation and stored under nitrogen prior to use. All other solvents used were reagent grade and were employed without further purification.

Monomer synthesis: 4,4'-dihydroxy-α,α'-dimethylbenzalazine was prepared according to the procedure of Blout et al.[10] by refluxing an ethanol solution of 0,45 molar equivalent hydrazine monohydrate with 4-hydroxyacetophenone and a catalytic amount of concentrated hydrochloric acid for 6-8 h. The azine separated out upon cooling the solution overnight, and was then filtered off and recrystallized from aqueous ethanol. Typical yields of the first set of yellow needle-shaped crystals were 75-85%; m. p. 225-226 °C (lit. 222-223 °C[10] ; 224 °C[11]).

^{1}H NMR (CDCl$_3$) : δ = 2,25 (s ; $\underline{CH_3}$-C=N-), δ = 6,80-6,83 and 7,75-7,78 (m ; p-phenyl), δ = 9,82 (s ; phenyl - O$\underline{H}$); integration ratios : 3 : 2 : 2 : 1.

C$_{16}$H$_{16}$N$_2$O$_2$ (268,3) Calc. C 71,62 H 6,01 N 10,44

Found C 71,89 H 6,19 N 10,43

Polymerisation: Interfacial polymerisation (Tab.1 ; reac. **1 & 2**) was carried out in a high speed Waring blender. The organic layer (dichloromethane ; 100ml) containing 5

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mmol of each sebacoyl and dodecanedioyl dichlorides was rapidly added to a slowly stirred aqeous layer (150ml) composed of 10 mmol of the azine diol, 1,2g sodium hydroxide and 0,25g butyltriethylammonium chloride. The mixture was then stirred at the highest speed for 5min. Pale yellow polymer was recovered by transferring the resulting slurry rapidly into methanol (500 - 1000ml) with vigorous stirring which was then filtered, further washed with aliquots of methanol, methanol/water and water and finally dried i. vac. at 60 -70°C for at least 24h.

Solution polymerization (Tab. 1&2) was carried out under nitrogen atmosphere in a three-neck round bottom flask (500 ml) equipped with an addition funnel, a reflux condenser and a mechanical stirring assembly according to the following general procedure: The diol (10-50 mmol) was dissolved in a solution of chloroform (20 - 150ml)) containing an excess of the acid acceptor (pyridine or triethylamine; 5-30ml) and, in some cases, a small amount of NMP (2-10 ml). The latter helped to dissolve the otherwise sparingly soluble azine in chloroform. An equivalent and sometimes a slight excess (< 1 mole%) of a 50/50 molar mixture of the sebacoyl/dodecanedioyl acid chlorides (10-50 mmol) in chloroform (30-50ml) was added to this solution over a period of 10 min-1,5 h. with vigorous stirring. The temperature was maintained between 0 - 60°C depending on the particular reaction conditions chosen (Tab.1 &2) and the solution was vigorously stirred for a further 3-4 h. After allowing the reaction mixture to cool down (if necessary), it was usually diluted with chloroform (ca. 50 ml) to reduce the viscosity. The products were then recovered by precipitation into methanol and were worked up as described above. In all cases the yields were near quantitative (Tab.1 & 2). The product from reaction 12 had the following elemental analysis.

$(C_{27}H_{32}N_2O_4)_n$ $(448,6)_n$ Calc.   C 72,30 H 7,19 N 6,25

Found C 72,31 H 7,30 N 6,23

^{1}H NMR see Fig.1 (A)

Measurements: ^1H NMR spectra were taken from $CDCl_3$ solutions with Me_4Si as the internal standard on a Bruker AC270 instrument (270MHz). IR spectra were recorded using a Nicolet 60SX Fourier-Transfrom IR Spectrometer from thin films of the polymer cast on KBr discs. Thermal transitions were determined using a Perkin Elmer DSC-7 Differential Scanning Calorimeter at 20^oC/min heating and 10^oC/min cooling rates on 5-10mg samples under nitrogen atmosphere. Likewise thermogravimetric analysis was also performed at 20^oC/min heating rate and under nitrogen atmosphere using a Perkin Elmer TGA-7 Thermogravimetric Analyser.

Solution viscosity measurements were carried out in chloroform at 25^oC using a Ubbelohde viscometer and [η] was expressed as η_{inh} at 0,5 g/dl concentration. In case of the polymers on which light scattering measurements were performed [η] values were determined using at least four different concentrations between 0,5-1,5 g/dl, followed by the usual extrapolation of η_{sp} and η_{inh} plots to a common intercept at $c = 0$.

Gel permeation chromatography (GPC) was carried out using a Waters Model 510 instrument , equipped with four Ultra Styragel (500, 2 x10^3, 10^4 A^o) columns and a Waters 490 Programmable Multiwavelength UV detector (250nm) using a 1ml/min flow rate and chloroform as the mobile phase. 100 μl injections were made of ca. 0,06% (w/v) chloroform solution of the polymers and the system was calibrated with polystyrene standards. The chromatographic data were collected and analysed using the Waters Expert Chromatography software (version 6.0).

Static light scattering (LS) experiments were performed with an Otsuka Electronics Photal DLS 700 Dynamic Light Scattering Spectrophotometer using a He-Ne laser (5mW) and 21mm cells. Measurements were made in chloroform solution (filtered through 0,2μm membrane filters) at 25 ± 1^oC using four different concentrations (ca. 1-4mg/ml) and 13 different angles (30-150°) for each polymer. Benzene was used as the

standard. An Otsuka Electronics Photal RM-102 Differential Refractometer (633nm) was used for dn/dc determinations. Scattering data were collected and Zimm plots were constructed using Otsuka Electronics DLS 700 software (version 2.11).

Elemental analyses were carried out by Galbraith Laboratories ,Inc., Knoxville Tannessee.

Results and discussion

Polymer synthesis

Initial attempts to prepare the polymer via an interfacial polymerisation unde. conditions similar to those described by Roviello and Sirigu[2,5] were abandoned as a result of erratic and poor reproducibility, as well as the inability to produce polymer of $\eta_{inh} > 0,75$ dlg^{-1} (Tab.1 ; reac. 1&2). Since this polymer is readily soluble in chlorinated solvents, especially chloroform, a solution polycondensation route was developed (Scheme 1). Tab.1 summarises the various reaction conditions that were tried. Inherent viscosity and the polystyrene equivalent $\overline{M}_w$ obtained from GPC as well as the absolute $\overline{M}_w$ calculated from light scattering data of the products are also included in Tab.1. 4,4'-dihydroxy-α,α'-dimethylbenzalazine was sparingly soluble in chloroform in the concentration range studied, but it readily dissolved when a small amount of NMP was added. When pyridine was used as the acid acceptor (reac. 3-6), a large excess of pyridine was also found to facilitate a homogeneous solution of the diol and, thus, NMP was later omitted from this system (reac. 4-6).

With the exception of reaction 6, only low molecular weight products were obtained with the pyridine system. It was intially thought that the polymer solubility could be improved by carrying out the polymerisation at room temperature with very slow addition of the acid chloride solution, reac. 3,4. However, no appreciable viscosity increase of the mixtures was observed in these experiments. Moreover, the polymer

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precipitated out progressively with time, which was believed to be the limiting factor for obtaining high molecular weight polymer. Increasing the reaction temperature to 60°C (including during acid chloride addition), reac. **5**, failed to improve the molecular weight significantly, even though the polymer remained in solution throughout. Scaling the reaction down to 20mmol at 60°C (reac. **6**),however, resulted in a high molecular weight polymer whose η_{inh} was comparable to that produced by the interfacial reactions. Why the pyridine-based system failed to yield high molecular weight polymers is not completely clear at this stage, but conceivably, it could have been due to some decomposition of the acid chlorides during the slow addition process.

Improved results were obtained when triethylamine was used as the acid acceptor, reac. **7-10**. In these experiments a small amount of NMP was also necessary to dissolve the diol and the acid chloride solution was added relatively faster (10-15min) and usually at 0°C. Efficient polymerisation was immediately apparent as, in reac. **7**, the solution became highly viscous at the end of the addition, and the product precipitated from solution. This particular reaction (**7**) was then allowed to warm to room temperature, but this failed to induce a homogeneous solution. Nevertheless, in spite of the precipitation, high molecular weight polymer was obtained (Tab.1). Running the reaction at room temperature, reac. **8**, and at higher concentration also gave similar observations, but a lower molecular weight polymer. The highest molecular weight polymer was obtained in reactions **9** and **10**, where the solutions became gel-like upon the completion of acid chloride addition (at 0°C), and the polymer precipitated within minutes after all the acid chloride was added.. Raising the temperature to 60°C resulted in a homogeneous solution that was still extremely viscous, implying high polymer. This scheme was scaled up to prepare 20-30g quantities of polymers with varying molecular weight, which was achieved by changing the stoichiometric balance of the reactants. Tab. 2 summarises these reactions and the product molecular weights. It was surprising

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that a relatively high molecular weight polymer was obtained when a 4 mol% excess of the acid chloride mixture was used (reac. **11**). This may be explained by the relatively slow rate of addition of the acid chloride solution, during which the stoichiometry of reactants passes through the equivalance point. Thus, given the rapid polymerisation, high molecular weight may be the result and the excess acid chlorides never participate in the reaction. When the role of the reactants was reversed, however, i.e. the diol in the bulk solution being in excess, (reac. **13 &14**) it was possible to suppress the molecular weight of the polymer in a controlled manner (Tab. 2).

Polymer characterisation

Structural evaluation of the products listed on Tab.1&2 were made by ^{1}H NMR and FTIR spectra, and their composition were based on elemental analyses (see. Exptl. Part.). ^{1}H NMR and IR spectra of the product from reaction **12** are given in Fig.1. The methylene protons adjacent to the carbonys appeared as a triplet at $\delta = 2.58$, $\beta-$ methylene protons appeared as multiplets at $\delta = 1.78$ while the remainder of methylenes clustered at $\delta = 1.35 - 1.41$. p-Substituted phenyl protons resonated further downfield as a multiplet at $\delta = 7.12 - 7.15$ and $\delta = 7.91 - 7.94$, whereas the methyl groups in the mesogen appeared as a singlet at $\delta = 2.30$. Integration ratios were in the order of 2 : 2 : 5 : 2 : 3 respectively, corresponding to an average of nine methylene groups per repeat unit, which is consistent with the 50 / 50 molar ratio of the two spacers. The IR spectrum, given in Fig.1, also confirmed the expected structure. Strong C -H stretching, C = O absorption, - C = C - ring stretching and C - H deformation (in p-substituted aromatic rings) bands occured at 2925 and 2851, 1757, 1600 and 1504, and 816 cm^{-1} respectively.

As-prepared polymers appeared to be highly crystalline since no appreciable T_g transition was visible on the first DSC heating thermograms. Representative samples

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of the 2nd DSC heating and cooling thermograms are given in Fig. 2. The polymer had a T_g ca. 25°C, a double endotherm between 150-160°C, the second of which was ascribed to the crystal - nematic transition (T_{K-N}), and a nematic - isotropic transition (T_{N-I}) at ca. 250°C. As seen in Fig. 2, the polymer is enantiotropic and exhibited appreciable supercooling of T_{K-N}. The nature of the endotherm preceeding T_{K-N} (denoted as T_1) is not fully understood yet; no significant change of the sample was observed in this region by hot stage polarising microscopy. Nevertheless, T_1 was reproducible during heating cycles, though its magnitude decreased as the cycles were repeated. A number of such transitions were also reported by Roviello and Sirigu[2,4,5,11] during their investigation of a series of polymers and model compounds based on this particular mesogen. The authors attributed these to crystal - crystal transitions. It is also believed in the present study that T_1 represents a solid state polymorphism. The crystalline phase of the polymer appeared to be highly stable since it was difficult to obtain an amorphous sample by quenching either from a nematic melt or an isotropic liquid.

The effect of molecular weight on thermal transitions is illustrated in Fig. 3. As expected, both T_{K-N} and T_{N-I} increased with increasing molecular weight, finally reaching a plateau at higher $\overline{M}_w$. The magnitude of the change was found to be greater for T_{N-I} than T_{K-N} and constant values were reached ca. $\overline{M}_w$ >20,000 (polystyrene equivalent $\overline{M}_w$ ca. 50,000-60,000). No appreciable change in the T_g of the polymer with $\overline{M}_w$ was observed.

The polymer possessed relatively good thermal stability. Thermogravimetric analysis (20°C/min; in N_2) indicated that the onset of thermal degradation was around 350°C. Prolonged heat treatment (>1h) at elevated temperatures (260 - 280°C), resulted in less than 2% weight loss. The molecular weight of the polymers after such treatments was found by GPC to decrease by less than 10%.

It was possible to obtain chloroform solutions of the polymer up to 10% (w/v) at room temperature for all molecular weights. No indication of lyotropic behaviour was observed. Initially, molecular weight estimations were made from solution viscosity and GPC measurements (Tab. 1&2). The latter were particular useful for determining the polydispersities, $\overline{M}_W/\overline{M}_n$, of the polymers, which in most cases were between 2-3. Much higher values were, however, exhibited by polymers prepared in pyridine-based reactions. In these cases, the GPC traces often contained low molecular weight tails. It was suspected that the "polystyrene equivalent" molecular weights were probably high, because of the differences in the hydrodynamic volume of these polymers and polystyrene. Thus light scattering measurements were also made, though it should be noted that these were performed 6 - 9 months after the synthesis of the polymers. During this time a small reduction in η_{inh} of some of the polymers was observed which was attributed to chain cleavage as a result of decomposition of residual acid chloride end groups. Light scattering measurements were carried out on eight polymers with $[\eta]$ ranging between 0,34 - 1,23 dlg^{-1} and with polydispersities (from GPC) of 2-3, (except for the lowest molecular weight polymer which had an $\overline{M}_W / \overline{M}_n$ of ca. 5,6). Typical examples of the relationship between the refractive index increment (Δn) vs concentration in the range employed and that of a Zimm plot are presented in Figs. 4 and 5. Good correlation between the measured $[\eta]$ and weight average molecular weights from Zimm plots (Fig. 6) was obtained, which allowed for the calculation of the Mark - Houwink - Sakurada relationship for this polymer-solvent system,

$$[\eta] = 9{,}6 \times 10^{-4} . \overline{M}_W^{0{,}68} \qquad (CHCl_3 ; 25^oC)$$

It appears that chloroform is a fairly good solvent for this polymer. The persistence length was calculated to be in the order of 27 A^o using the procedure of

Bohdanecky[12] which is based on a theory by Yamakawa and Fuji[13]. More detailed light

scattering studies on the fractionated samples of the polymer are currently in hand and

will be reported in the future.

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Legends to Figures

Fig. 1. (A) ^{1}H NMR and (B) FTIR spectra of the copolymer prepared in reac. **12**

Fig. 2. DSC (A) second heating (20°C/min) and (B) cooling (10°C/min) thermograms of the copolymer (from reac. **7**)

Fig. 3. Effect of the molecular weight on the thermal transition of the copolymer

Fig. 4. Refractive index increment against concentration for the copolymer (from reac. **10**) in chloroform

Fig. 5. Zimm plot for the copolymer (from reac. **10**) measured in chloroform at 25°C

Fig. 6. Viscosity-molecular weight relationship for the copolymer in chloroform at 25°C

Tab. 1. Synthesis of the copolyester of 4,4'-dihydroxy-α,α'-dimethylbenzalazine and sebacoyl / dodecanedioyl dichlorides (50/50 mol%) under various conditions.

Reaction [a]	Diol in mmol [b]	Solvent in ml	T/°C	Yield in %	$[\eta]$ [g] /dlg−1	$\overline{Mw}$ GPC [h] x10⁻⁴	$\overline{Mw}/\overline{Mn}$ [i]	LS [j] x10⁻⁴
		CH₂Cl₂ / H₂O						
1 [c]	10	100/150	RT	89,7	0,67	5,33	2,6	1,58
2 [c]	10	100/150	RT	87,5	0,75	-	1,9	1,80
		Py / NMP / CHCl₃ [d]						
3	25	5 / 10 / 100	RT	94,7	0,27	0,80	9,6	0,41
4	25	15 / - / 100	RT	95,2	0,32	1,28	5,9	0,53
5	35	25 / - / 100	60	97,5	0,36	1,61	3,0	0,63
6	20	15 / - / 100	60	98,7	0,67	5,38	2,7	1,58
		(CH₃CH₂)₃N / NMP / CHCl₃						
7 [e]	15	5 / 10 / 100	0	97,8	0,95	9,50	2,8	2,64
8	30	10 / 10 / 100	RT	98,1	0,78	6,79	2,7	1,97
9 [f]	25	15 / 5 / 100	0	98,5	1,46	18,98	2,4	4,97
10 [f]	10	6/2/50	0	98,0	1,56	20,30	2,3	5,48

a) Acid dichlorides were added from chloroform solution over a period of 1-1,5 h in pyridine and 10-15 min in triethylamine system, and reactions were allowed to proceed for a further 4 h

b) 50/50 mol ratio of -(CH₂)₈ - and -(CH₂)₁₀ - acid dichlorides were used to make up the equivalance

c) Interfacial reaction : Aqueous layer contains 1,2g NaOH and 0,25g butyltriethylammonium chloride ; reaction time : 5min

d) Py = Pyridine ; NMP = N-methylpyrrolidone

e) Reaction was carried out at room temperature after the addition of acid chloride solution

f) Reaction was heated to 60°C after the addition of acid chloride solution

g) Measured at c = 0.5 gdl⁻¹ chloroform at 25°C.

h) Expressed as "polystyrene equivalent" from gel permeation chromatography

i) From GPC

j) Calculated from the relation ship $[\eta] = 9,6\times10^{-4} \cdot \overline{Mw}^{0,68}$, obtained from light scattering

Tab. 2. Effect of changing the stoichiometric equivalence of reactants on the molecular weight of the copolyester of 4,4'-dihydroxy-α,α'-dimethylbenzalazine and sebacoyl / dodecanedioyl dichlorides (50/50 mol%)

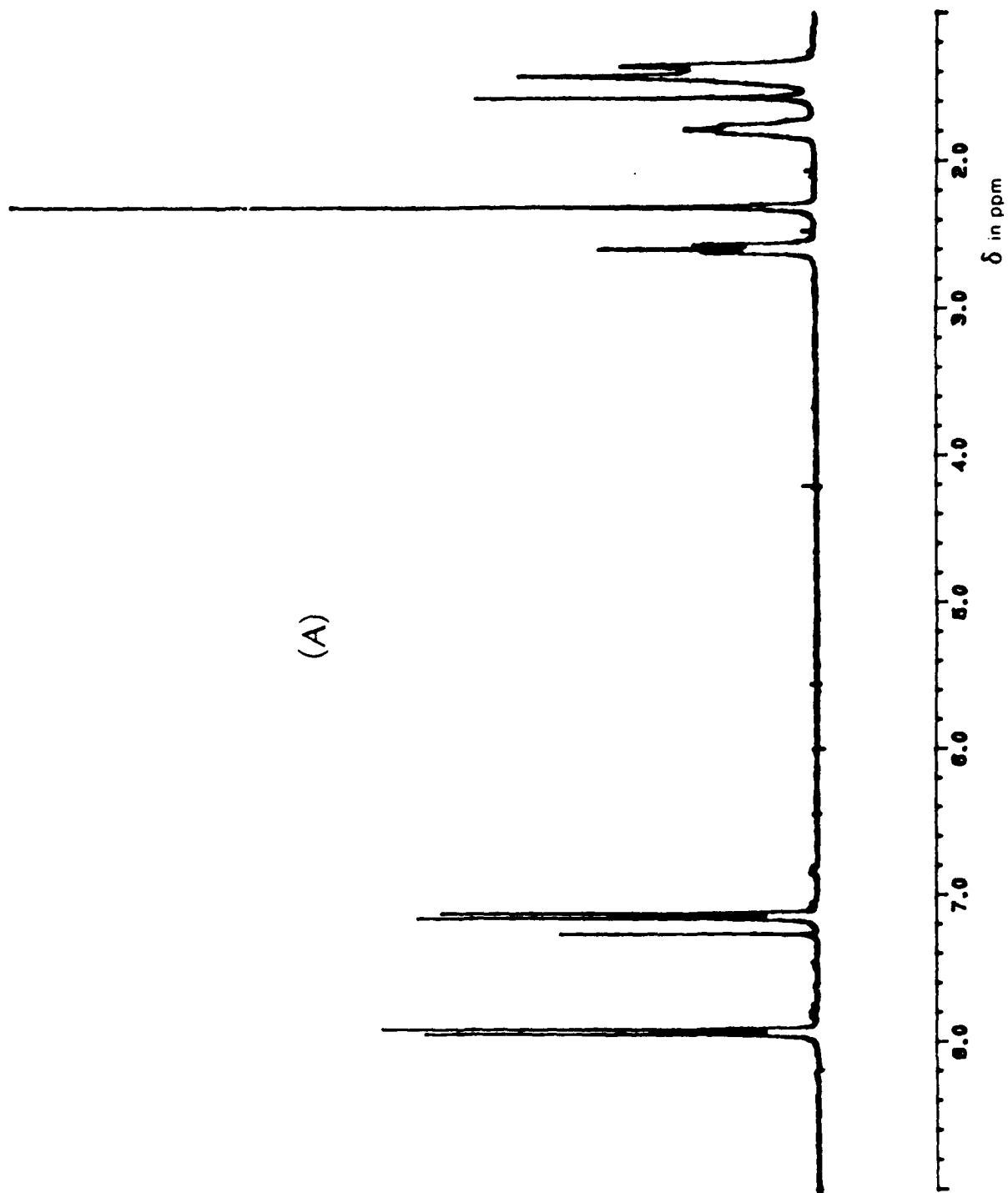| Reaction[a]	Excess diol in mol%	Yield in %	$[\eta]$[b] /dlg⁻¹	$\overline{M}w$		
				GPC[c] x10⁻⁴	$\overline{M}w / \overline{M}n$[d]	LS[e] x10⁻⁴
11	-4	98,8	1,45	15,21	2,2	4,92
12	0	98,2	1,32	13,73	2,3	4,29
13	2	97,7	0,88	7.03	2,3	2,36
14	4	95,4	0,61	3,81	2,4	1,37

a) Reaction conditions : 50 mmol of diol, 25 mmol of each sebacoyl and dodecanedioyl dichlorides, 30 ml triethylamine, 5 ml NMP, 200 ml chloroform ; 0°C during addition of acid chlorides ; 3 h at 60°C.
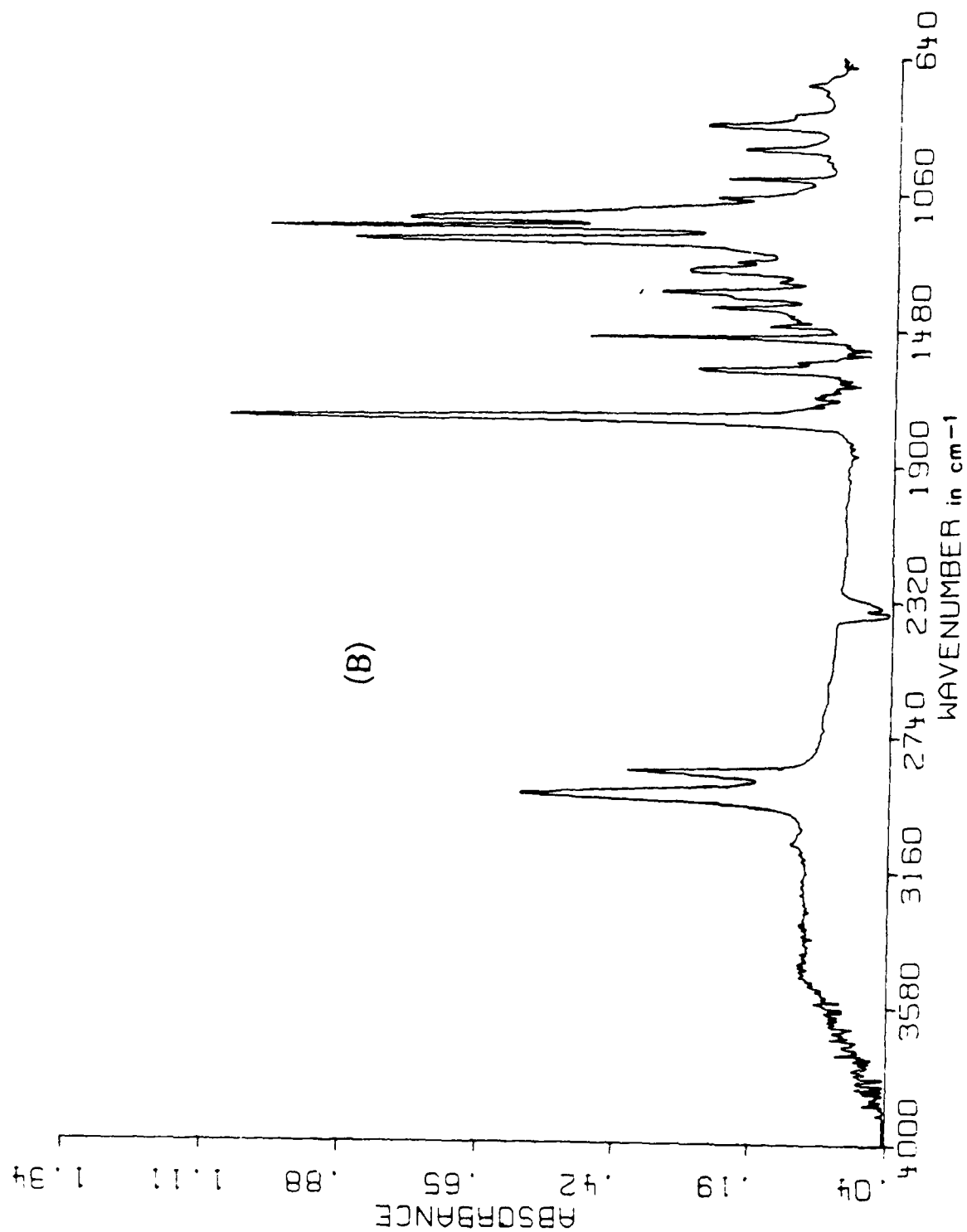
b) Measured at c = 0.5 gdl⁻¹ in chloroform, 25°C.

c) Expressed as "polystyrene equivalent" from gel permeation chromatography

d) From GPC

e) Calculated from relationship $[\eta] = 9,6 \times 10^{-4} \cdot \overline{M}w^{0,68}$, obtained from light scattering

(A)

δ in ppm

(B)

Heat Flow / (wg⁻¹) vs T /°C

Curve (A) labels: T_g, T_1, T_{K-N}, T_{N-I}
Curve (B)

$10^4 \cdot \Delta n$

$10^3 \cdot c \,/\, (gml^{-1})$

10

8

6

4

2

0

0   0,8   1,6   2,4   3,2   4,0   4,8

$10^5 \cdot K_c / R_\theta$

$\sin^2(\theta/2) + 10.c$

Scheme 1

HO—C₆H₄—C(CH₃)=N—N=C(CH₃)—C₆H₄—OH

$$HO-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\overset{CH_3}{\underset{}{C}}\!=\!N-N\!=\!\overset{CH_3}{\underset{}{C}}\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-OH$$

+

$$\left\{\begin{array}{l} Cl-\overset{O}{\underset{\parallel}{C}}-(CH_2)_8-\overset{O}{\underset{\parallel}{C}}-Cl \\[2mm] Cl-\overset{O}{\underset{\parallel}{C}}-(CH_2)_{10}-\overset{O}{\underset{\parallel}{C}}-Cl \end{array}\right.$$

⟶

$$\left[-O\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\!\overset{CH_3}{\underset{}{C}}\!=\!N-N\!=\!\overset{CH_3}{\underset{}{C}}\!\!-\!\!\left\langle\bigcirc\right\rangle\!\!-O-\left\{\overset{O}{\underset{\parallel}{C}}-(CH_2)_8-\overset{O}{\underset{\parallel}{C}}\right\}_{0-5}\left\{\overset{O}{\underset{\parallel}{C}}-(CH_2)_{10}-\overset{O}{\underset{\parallel}{C}}\right\}_{0-5}\right]_n$$
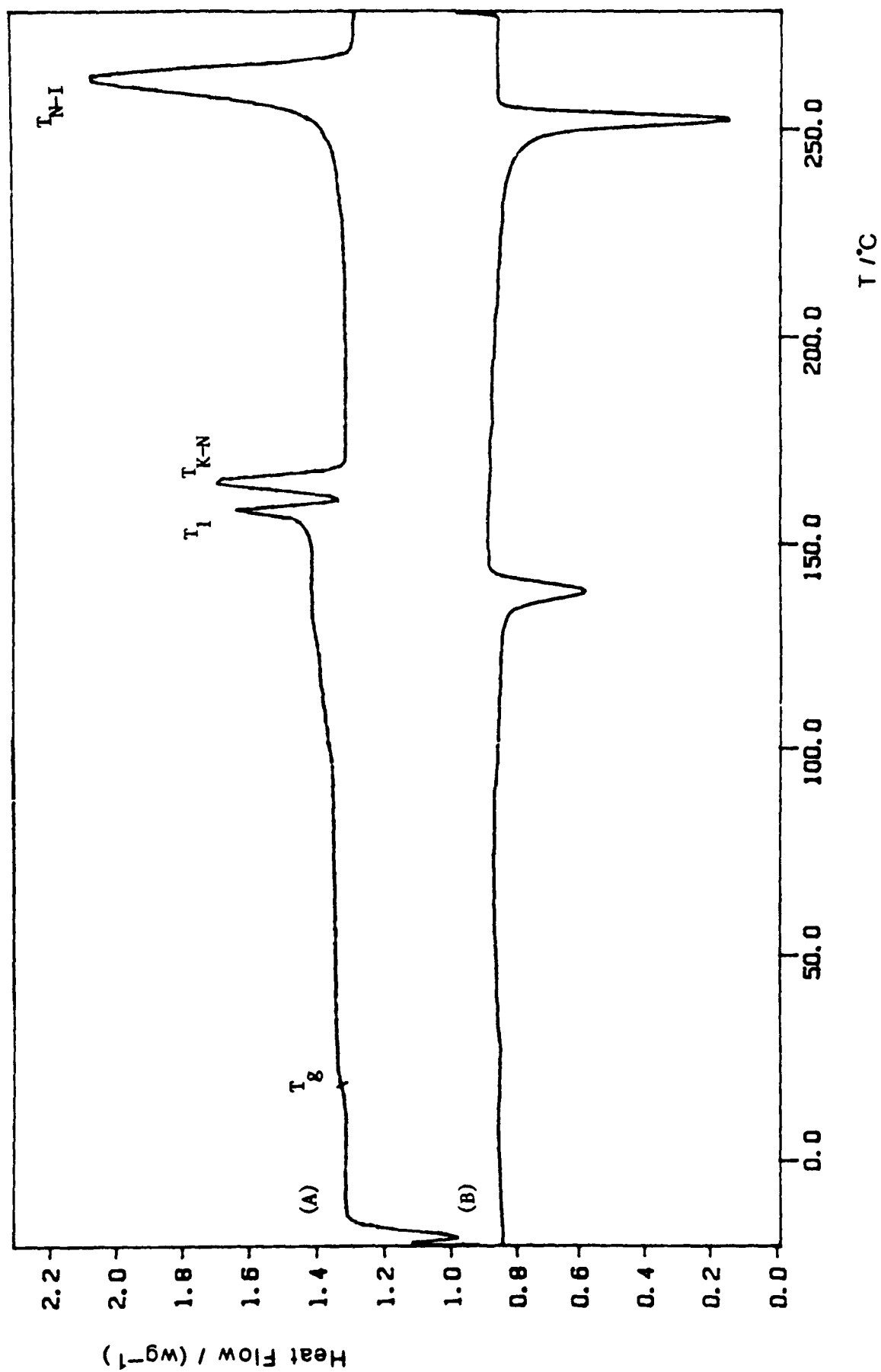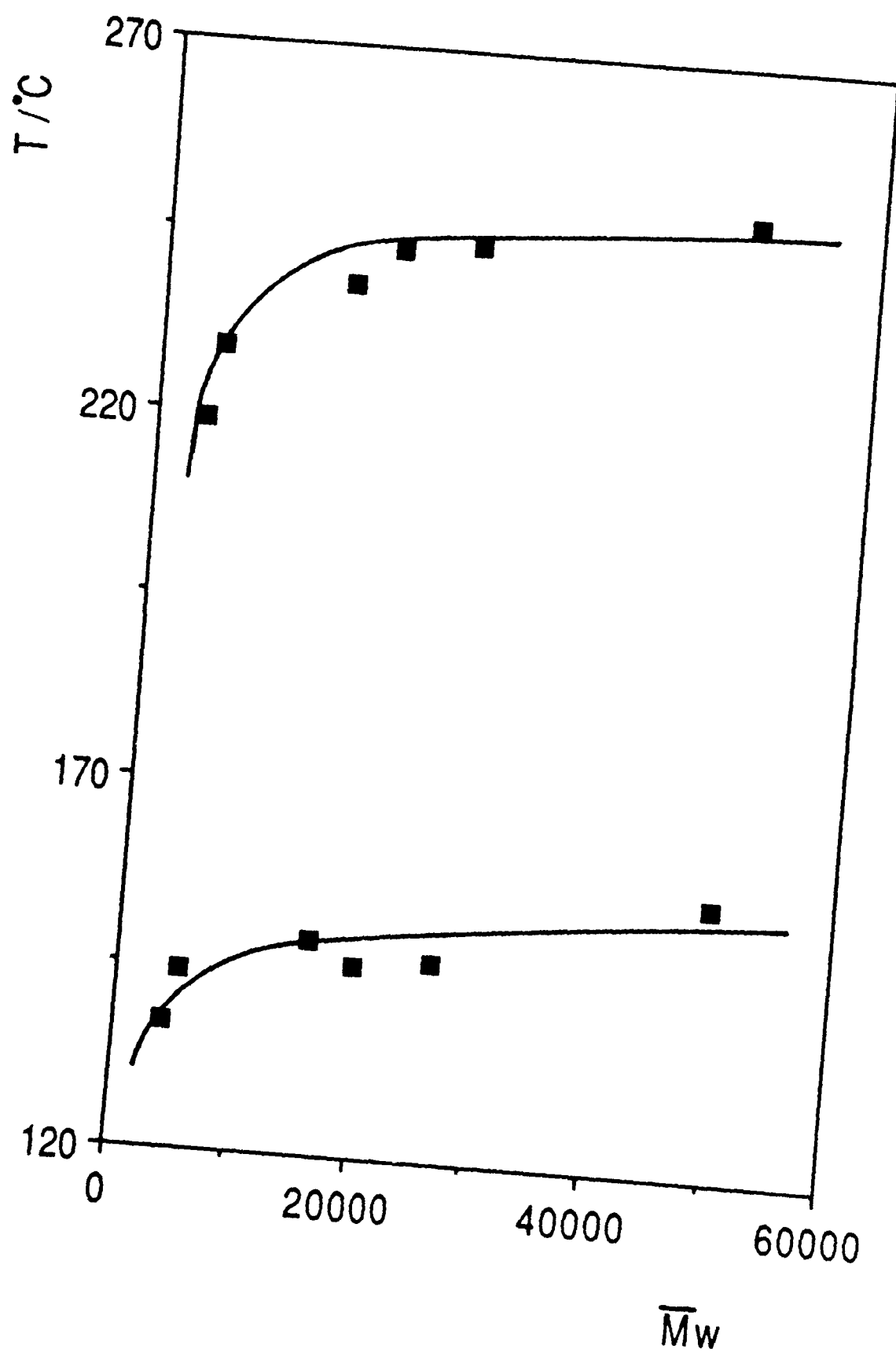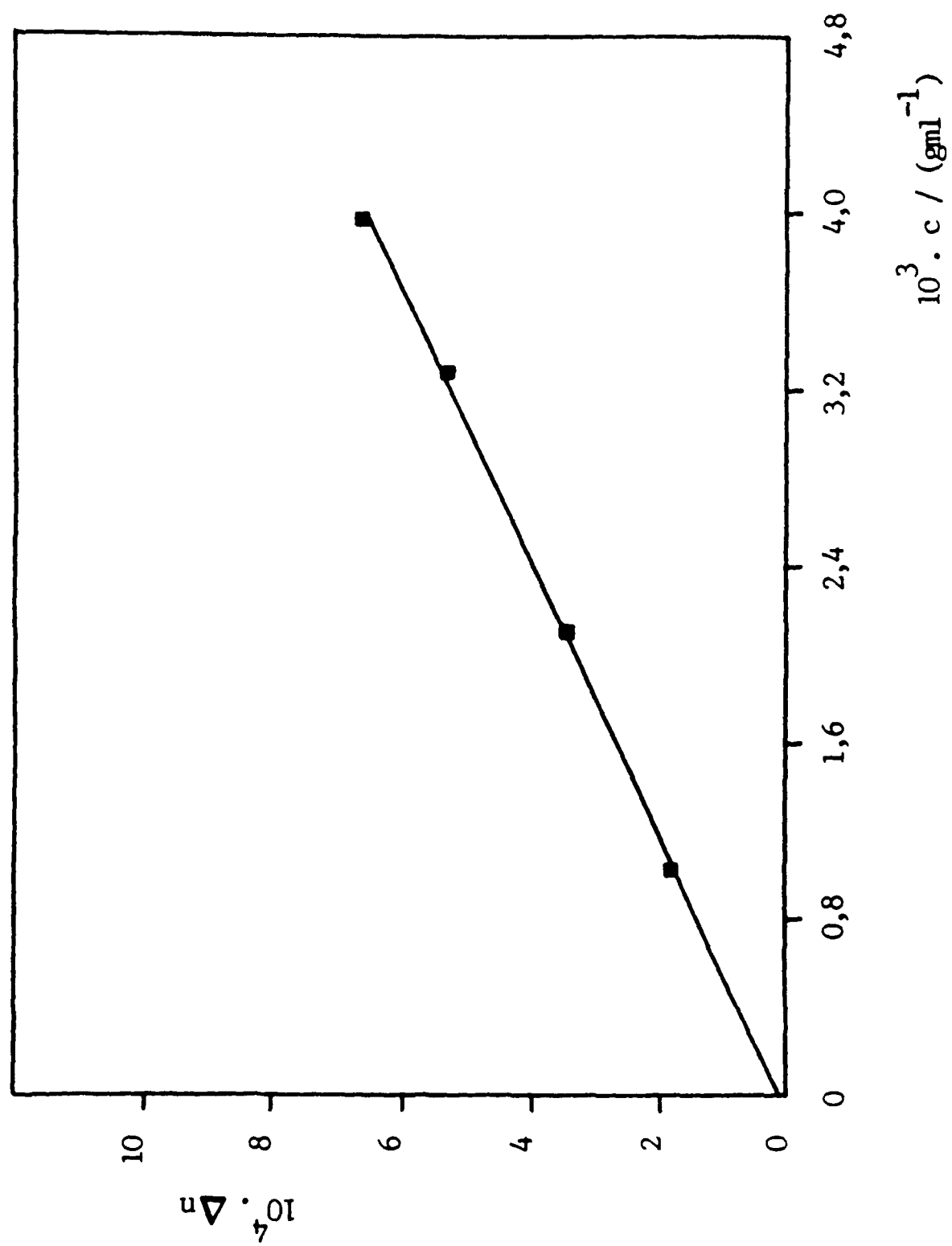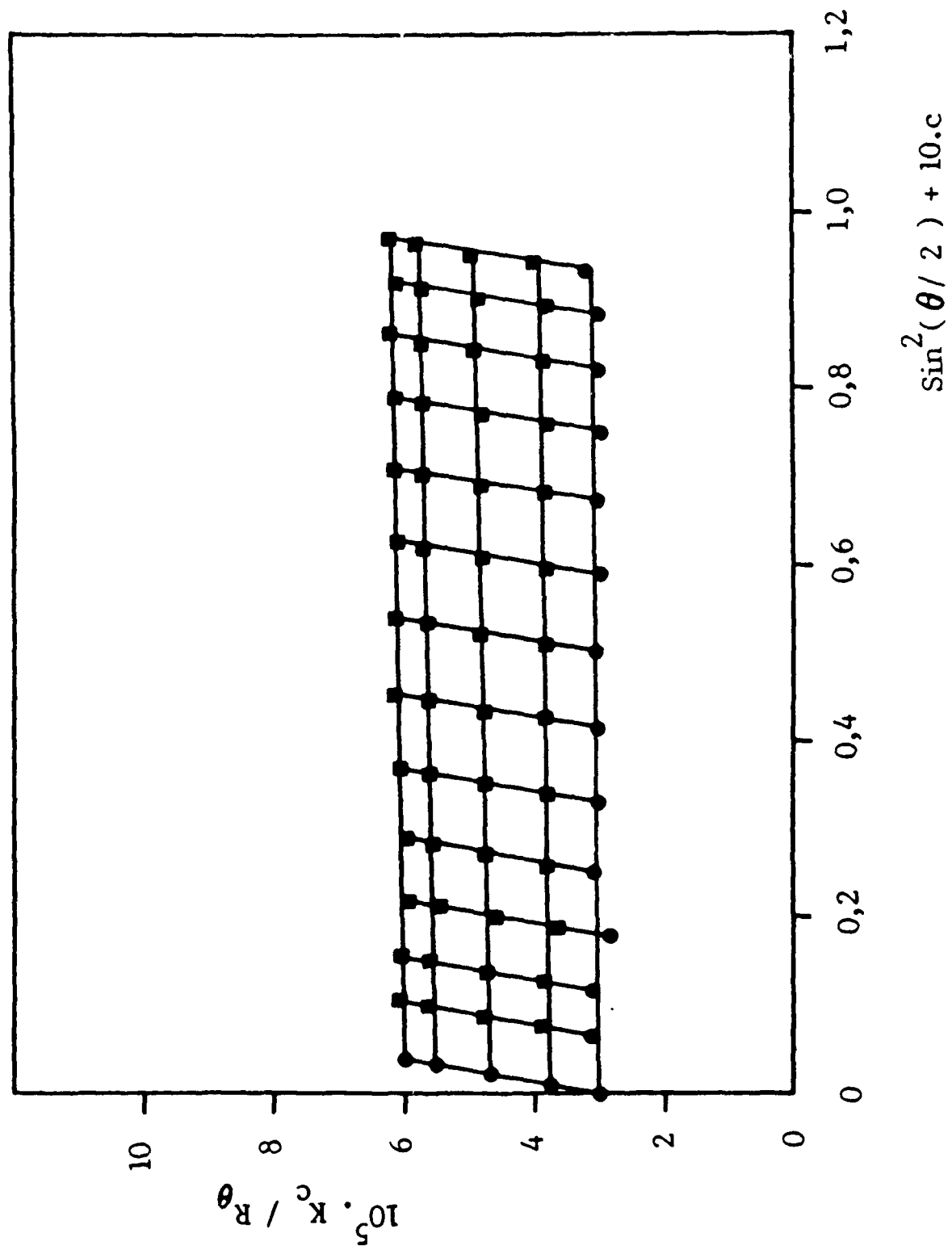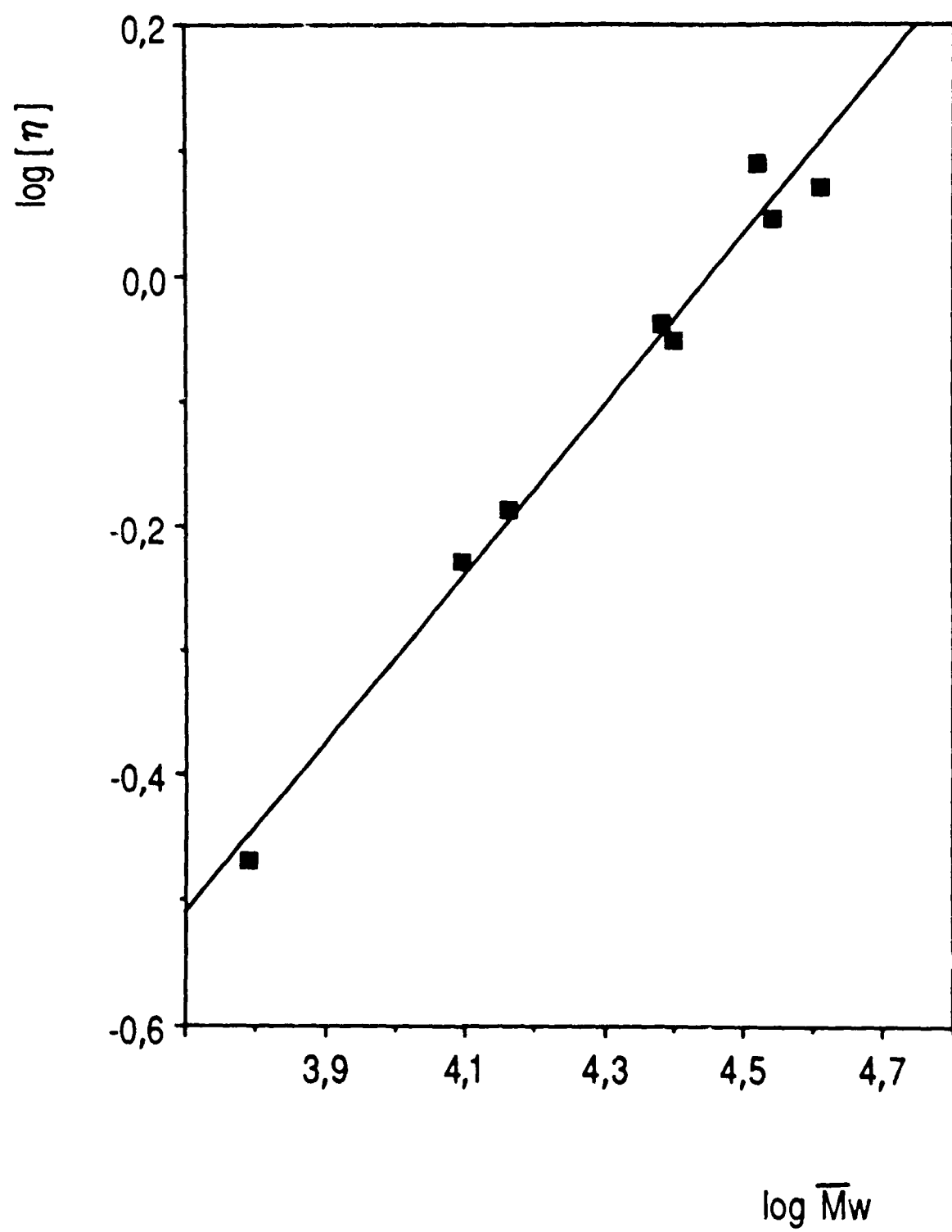
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